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Fe³⁺ and Fe²⁺ Partitioning among Silicates in Metapelites: A Synchrotron Micro-XANES Study

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Beamline(s): X26A

Introduction: At present the only true microscale technique for quantitative mineral analyses of Fe³⁺/ΣFe on unmodified thin sections is *Synchrotron microXANES* (SmX) spectroscopy (XANES is X-ray Absorption Near-Edge Structure). Extensive development work over the last decade has repeatedly tested this technique on grain mounts of individual minerals for which wet chemical and/or Mössbauer data were previously available. With the mineral group-dependent uncertainty of the method established to be roughly ±3-10%, the technique can now be applied to the study of minerals in thin sections, allowing petrologic context to aid in the interpretation (and understanding) of the results.

Accordingly, we use here metapelite samples from the well-studied occurrences in western Maine to allow consideration of our results within a tightly constrained petrologic framework in which the effects of pressure (P), temperature (T), fluid phase composition, and mineral assemblage can be taken explicitly into consideration. Because of the petrologic context, our results have direct applicability and significance for studies aimed at the petrogenesis of common metapelitic rocks. Moreover, it should be possible to relate these results to petrologic controls, especially T and fluid composition during crystallization of the minerals. Thus, the goal of this work is to study Fe in minerals in metapelites over a range of temperatures from lower garnet zone to K-feldspar+sillimanite zone conditions with a range of mineral assemblages representing f_{O_2} from graphite/ilmenite to magnetite-hematite-bearing rocks. Once completed, this program of study will also enable formulation of expressions for estimating compositional variables such as Fe³⁺ and H⁺ in minerals from similar metapelitic rocks in which such detailed characterizations are not available.

Methods and Materials: Synchrotron micro-XANES spectroscopy (SmX) was used to measure Fe³⁺ and Fe²⁺ distribution among minerals in standard thin sections with an X-ray beam size of 10x15 μm. Measurements were made at Beamline X26A, National Synchrotron Light Source, Brookhaven National Lab. Samples studied included metapelites from garnet to upper sillimanite zone rocks that coexist with graphite, graphite/ilmenite, or varying combinations of ilmenite, magnetite and hematite. SmX results are compared with Mössbauer spectroscopic measurements of Fe³⁺ on mineral separates from the same rocks.

Results: Results show excellent agreement (within ±5-10%) between Mössbauer and SmX for the Fe-rich phases biotite, chlorite, staurolite, and garnet. Mössbauer spectra of muscovite typically show lower values than SmX for Fe³⁺/ΣFe (especially at low grades), suggesting contamination of the muscovite separates by fine-grained chlorite. However, heterogeneity of Fe³⁺ and Fe²⁺ is probably the chief source of discrepancy between the bulk and micro-scale measurements. The %Fe³⁺ (relative to total Fe) in these samples ranges from a high of 90% in muscovite to a low of 0-2% in garnet, with Ms>St=Bt=Chl>Tur>Grt in graphite/ilmenite-bearing rocks.

SmX measurements suggest that the averaged Fe³⁺/ΣFe in each mineral species does not change as a function of grade, but varies as a function of buffering assemblage, especially on a very localized scale. This effect shows that the oxygen buffering capacity of mineral assemblages is very large compared to the oxidizing/reducing potential of metamorphic fluids. However, distribution of Fe atoms among phases at each grade also reflects crystal chemistry. Across all grades, the Fe²⁺/Mg ratio is such that Grt >> St > Bt > Chl > Tur > Ms. Fe³⁺/Al is highest in biotite in garnet and sillimanite-zone rocks. For Fe³⁺/Al, Bt > Chl > Tur > St > Ms, and for Fe³⁺/Fe²⁺, partitioning behaves as Ms >> Bt ≈ St ≈ Chl > Tur > Grt in graphite/ilmenite-bearing rocks. Overall, partitioning of Fe³⁺ in any of the minerals of interest reflects both oxide assemblage and crystal chemical constraints on the amount of Fe³⁺ that can be substituted into the structure.

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